Solubility prediction of weak electrolyte mixtures

Gilles Févotte, Xiang Y. Zhang, Gang Qian, Xing-Gui Zhou, Wei-Kang Yuan

TITLE: SOLUBILITY PREDICTION OF WEAK ELECTROLYTE MIXTURES

Xiang-Yang Zhang, Gilles Févotte[a], Gang Qian, Xing-Gui Zhou, Wei-Kang Yuan

Dip. State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, China (zxydcom@mail.ecust.edu.cn)
[a] Dip. Ecole Nationale Supérieure des Mines de Saint Etienne, Saint-Étienne, France

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The solubility of materials is a thermodynamic variable that depends on their chemical composition and with temperature. Solubility is also affected by the pH, by the presence of additional species in the solution, and by the use of different solvents. On electrolyte, the calculation of solubility requires that the mean ionic activity coefficient be known along with a thermodynamic solubility product. [1-3]

When an electrolyte is dissolved in water, the dissociation reaction can be written as

$$M_{\upsilon+}N_{\upsilon-}(s) \Leftrightarrow \upsilon_+ M^{z+} + \upsilon_- N^{z-} \tag{1}$$

where $z+$ and $z-$ represent number of charges on the cation or anion, υ_+ and υ_- are the stoichiometric number of ions of each type present in a given electrolyte.
As shown in Eq. (1), the solubility product, K_{sp}, is given by equation

$$K_{sp} = \alpha_{M^{z+}}^{\upsilon_+} \cdot \alpha_{N^{z-}}^{\upsilon_-} = (\gamma_{M^{z+}} m_{M^{z+}})^{\upsilon_+} (\gamma_{N^-} m_{N^-})^{\upsilon_-} = \gamma_\pm^{\upsilon} \cdot m_\pm^{\upsilon} \tag{2}$$

and

$$\upsilon = \upsilon_+ + \upsilon_- \tag{3}$$

where α denotes the activities of the species, $\gamma_\pm$ and $m_\pm$ represent the mean activity coefficient and the mean concentration of ions at equilibirum state in molal unit, respectively.

For strong electrolyte, the mean ionic concentration of ions in solution, $m_\pm$, can be written as a function of concentration of solute c

$$m_\pm = (m_{M^{z+}}^{\upsilon_+} \cdot m_{N^{z-}}^{\upsilon_-})^{1/\upsilon} = \left(\upsilon_+^{\ \upsilon_+} \cdot \upsilon_-^{\ \upsilon_-}\right)^{1/\upsilon} c \tag{4}$$

As to the mean ionic activity coefficient presented in Eq. (2), a number of methods are available. [4-7]

While the present methods are not available for the calculation of weak electrolyte, which is commonly involved in industry crystallization. In this paper, an approach to predict the solubility of pure weak electrolyte was proposed. Further, this approach was extended to predict the solubility of weak electrolyte mixtures.

In the case of weak electrolytes, the partial dissociation can be considered to be part of the association of anions and cations after totally dissociation. [8] Assuming the degree of dissociation is δ, and the chemical formulas of solute and association are $M_{\upsilon+}N_{\upsilon-}$ and $M_{n+}N_{n-}$, respectively. The consumption of cations and anions by forming the association in the solution can be calculated to be $(1-\delta)\upsilon_+c$ and $(1-\delta)\upsilon_+cn_+/n_-$, respectively. Given this situation, the 'real' mean concentration and activity coefficient of ions in solution can then be rewritten as

$$m_{\pm}' = \left\{(\upsilon_+\delta)^{\upsilon_+}[\cdot\upsilon_- - (1-\delta)\upsilon_+ n_- / n_+]^{\upsilon-}\right\}^{1/\upsilon} \cdot c \tag{5}$$

$$\gamma_{\pm} = \left\{\delta^{\upsilon_+}[\cdot 1 - (1-\delta)\upsilon_+ n_- / \upsilon_- n_+]^{\upsilon_-}\right\}^{1/\upsilon} \gamma_{\pm}' \tag{6}$$

where $m_{\pm}'$ and $\gamma_{\pm}'$ represent the 'real' mean concentration and activity coefficient of ions in solution. The degree of dissociation of many substances in aqueous solution are available in Lange's Handbook of Chemistry. [9] In the absence of available data, it can be obtained by monitoring the conductivity of unsaturated solution. As to the mean ionic activity coefficient, Bromley's model was used in our work.

The approach was valided by predicting the solubility of pure zinc lactate and zinc lactate in the presence of NaCl, HCl and three other generic organic acid including succinic acid, citric acid and malic acid. The results show that the approach gives a good agreement with experimental data (see Figures 1, 2 and 3).

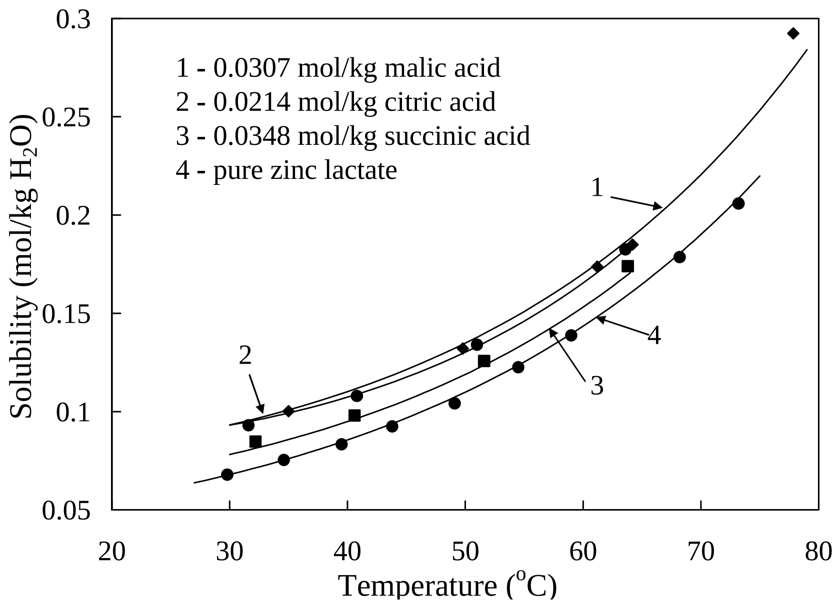

Fig.1. Solubility of pure and impure zinc lactate as a function of temperature .

Marks: experiments; [10] *Lines: calculated solubility*

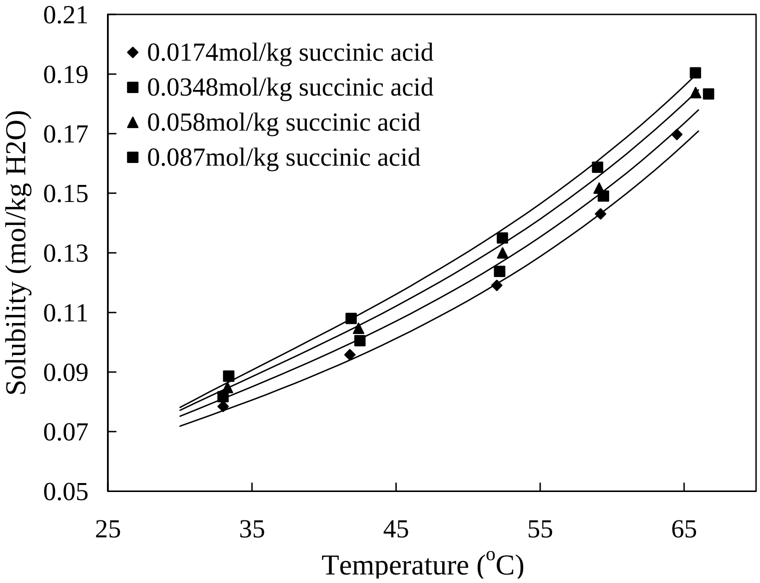

Fig.2. Solubility of zinc lactate as a function of temperature at different succinic acid concentration
Marks: experiments; [10] *lines: calculated solubility*

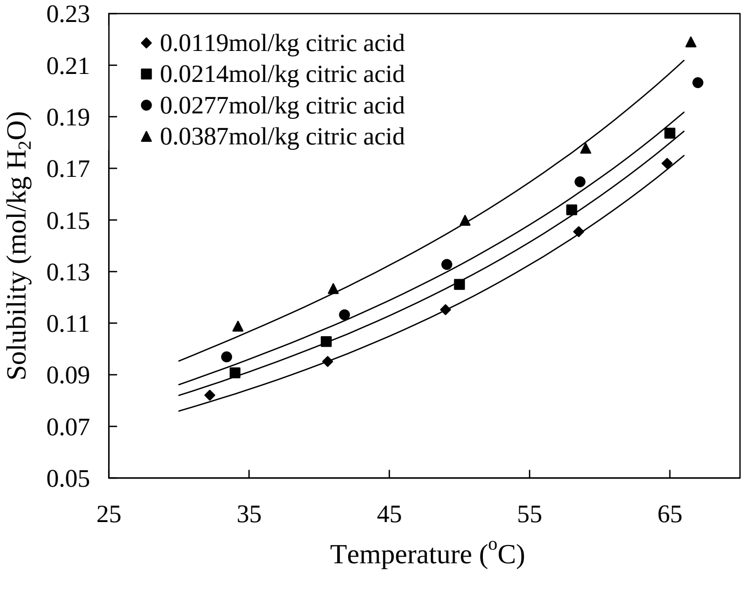

Fig.3. Solubility of zinc lactate as a function of temperature at different citric acid concentration.
Marks: experiments; [10] *lines: calculated solubility*

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